Supporting Information for:
Poly(glycidyl methacrylate)s with controlled molecular weights as low-shrinkage resins for 3D multibeam interference lithography
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1. Atom-transfer radical polymerisation of glycidyl methacrylate
Representative Procedure (for DPth.=30). Anisole (3.5 mL), freshly distilled glycidyl methacrylate (2.00 mL, 14.7 mmol), and 2-bromoproponitrile (50 μL, 0.58 mmol) were added by syringe to a mixture of CuBr (83 mg, 0.58 mmol) and 4,4'-dinonyl-2,2'-dipyridyl (600 mg, 1.46 mmol) under nitrogen at room temperature. The mixture was then heated at 60 °C under nitrogen for 12 h and then allowed to cool down to room temperature; the green solution was filtered through a silica gel plug to remove the copper-containing materials. The colorless filtrate was concentrated under reduced pressure; the residue was then dissolved in 3 mL of THF and precipitated out in ligroin to yield a white solid (1.25 g, yield: 60%). 1H NMR (400 MHz, CDCl3) δ 4.27 (bs, 1H), 3.78 (bs, 1H), 3.20 (s, 1H), 2.81 (s, 1H), 2.60 (s, 1H), 1.93-1.86 (m, 2H), 1.30-0.60 (m, 3H) (see also Figure S1). Polymers with different degrees of polymerisation were obtained in the same way but with the following ratios of monomer:initiator: 20:1, 30:1, 35:1, 45:1, 55:1 and 105:1. Table S1 summarises the molecular weight data for the polymers obtained from GPC in THF, while a representative GPC trace is shown in Figure S2.
Table S1. GPC data (THF) of PGMA samples prepared by ATRP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DP</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
</tr>
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<tr>
<td>1</td>
<td>20</td>
<td>3200</td>
<td>4400</td>
<td>1.34</td>
</tr>
<tr>
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<tr>
<td>4</td>
<td>55</td>
<td>7900</td>
<td>10000</td>
<td>1.27</td>
</tr>
<tr>
<td>5</td>
<td>105</td>
<td>15000</td>
<td>21000</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Figure S1. $^1$H NMR spectrum of poly(glycidyl methacrylate) (DP = 30) in CDCl$_3$. Note that the observed ratio of the peak areas of (a), (d) and (e) is about 3:1., indicating that the epoxy groups in the PGMA remain intact during the polymerisation of the GMA.$^1$

Figure S2. GPC trace of poly(glycidyl methacrylate) (DP = 30) in THF.
2. Details of diamond-like structure fabrication

Details for SU8 Structures. The 3D SU8 structures were fabricated by using the same set-up as that for the PGMA material. The photoresist solution (ca. 58 wt%) was formulated by mixing SU8 and 2.0 wt% Irgacure 261 (from Ciba Specialty Chemicals) as visible photoinitiators in γ-butyrolactone (Aldrich), and spin-coated on glass substrate at 2000 rpm for 30 s. The film was exposed to the superimposed interference beams (laser output of 1W) for ca. 1–2 s after soft baking. After post-exposure bake at 65 °C for 2 min and 95 °C for 2 min, respectively, the film was developed in propylene glycol monomethyl ether acetate (PGMEA, from Aldrich) to remove unexposed or weakly exposed materials, resulting in 3D microporous structures. To prevent the pattern collapse of the 3D porous film due to the capillary force during air-drying, we dried the film in a supercritical CO₂ dryer (SAMDRI-PVT-3D, tousimis) after the development.

Figure S3. SEM of diamond-like SU8 structures: a) large field of view, b) top view, and c) cross-sectional view.

Figure S4. Another SEM image of a 3D PGMA structure in cross sectional view after ion milling (sample tilted at 45 °).

3. Determination of epoxy cross-linking conversion

The cross-linking conversion of the epoxy groups was determined for the example with DP = 55 using IR spectroscopy. The absorption at 1737 cm⁻¹, assigned to the C=O stretching of the ester groups, should not change during the cross-linking, and was, therefore, used as an internal standard for quantification. The decrease of the band at 910
cm⁻¹ can be attributed to the polymerization of the epoxy groups and so the conversion of the epoxy group was determined by the Beer-Lambert law from the normalized changes of absorbance at 910 cm⁻¹ in Figure S5:

\[
\alpha_{\text{epoxy}} = 1 - \left( \frac{A_{910}^t}{A_{910}^0} \right)
\]

where \( A_{910}^0 \), \( A_{910}^t \) are the normalized absorbance of the epoxy group before curing, after exposure time \( t \) respectively.²⁻⁴ Our experimental data show that only about 7~10% epoxy groups were converted and polymerized after the PEB process. For different exposure time, the epoxy conversions are almost the same as shown in Figure S6.

**Figure S5.** FTIR spectra of PGMA (DP=55) before and after flood exposure to laser light at the same intensity as the MBIL process for different times.
Figure S6. Normalized FTIR absorbance of the epoxy group after different exposure times.

4. References for Supporting Information